

12

EUROPEAN PATENT APPLICATION

21 Application number: 88304837.3

51 Int. Cl.⁴: **C 23 C 14/32**
C 23 C 14/56
// A44C21/00

22 Date of filing: 27.05.88

30 Priority: 29.05.87 CA 538430

43 Date of publication of application:
30.11.88 Bulletin 88/48

84 Designated Contracting States:
AT BE CH DE ES FR GB GR IT LI LU NL SE

71 Applicant: **INCO LIMITED**
Royal Trust Tower Toronto-Dominion Centre
Toronto Ontario, M5K 1N4 (CA)

72 Inventor: **Bell, James Alexander Evert**
3217 Shoreline Drive
Oakville Ontario, L6L 5Y9 (CA)

Conard, Bruce Randolph
153 Balsam Drive
Oakville Ontario, L6J 3X4 (CA)

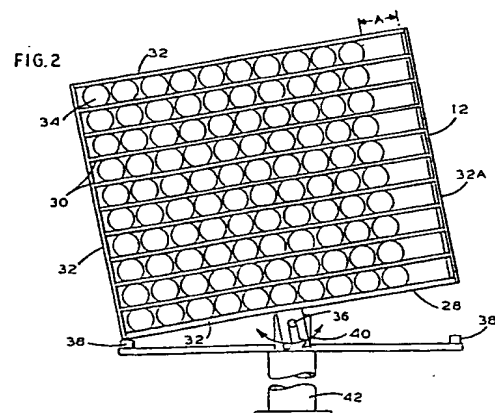
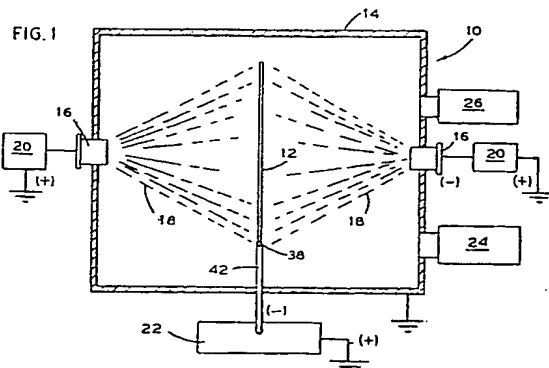
Babjak, Jura
671 Louis Drive
Mississauga Ontario, L5B 2V4 (CA)

Bradford, Raymond Augustus
216 Andrew Park
Woodbridge Ontario, L4L 1G5 (CA)

74 Representative: **Hedley, Nicholas James Matthew et al**
T.Z. Gold & Company 9 Staple Inn
London WC1V 7QH (GB)

64 Apparatus and process for coloring objects by plasma coating.

57 A technique is provided for presenting and fixturing small items that are coated by vapor deposition techniques. The objects (34) are held in a rack (12) that is held in a plasma stream (18). The objects are caused to be moved within the rack (12) to effect full coverage by the plasma stream. The coating, if titanium nitride, is gold colored and is, for example, useful for coinage applications.



Description

APPARATUS AND PROCESS FOR COLORING OBJECTS BY PLASMA COATING

TECHNICAL FIELD

The instant invention relates to coating objects in general and, more particularly, to a process for coating large quantities of mass produced metallic objects, such as coins, ball bearings, keys, etc. with a corrosion and wear resistant protective colored film by employing physical or chemical vapor deposition ("PVD" or "CVD") techniques.

BACKGROUND ART

For some time it has been known that highly corrosion and wear resistant films may be deposited on metallic surfaces by a number of PVD or CVD processes. Common applications include aerospace, nuclear and tool materials. Indeed the gold colored, premium cost, tools available to industry and consumers generally have a thin surface layer of titanium nitride (TiN) applied onto them by PVD techniques. TiN has demonstrably increased the lifetime of drilling and cutting tools several times when compared to similar non-coated tools.

Various substances, such as TiN, TiC, ZrN, HfN, TaN, TiAlN, TiO₂, ZrO₂, HfO₂, Ta₂O₅, etc. have been synthesized by vapor deposition processes as coating materials. These materials exhibit a number of special properties.

Tools or larger parts are exclusively coated by a batchwise PVD technique. The parts are placed in a reactor on a table-like fixture and then coated. In some cases the parts are placed in a Christmas tree-like fixture mounted on a rotatable table. Loading and unloading of parts is thus labor intensive. Accordingly, table-type fixturing devices are preferred to be used in the coating of relatively expensive parts. The cost for table-fixture coating these parts might appear quite high in absolute terms but is not too significant in relation to the total cost of the parts. For example, coating costs of 0.50 cents per piece that normally sell for 10 may be a tolerable expense. However, the same coating cost cannot be justified for parts of very low cost.

Accordingly, vapor deposition technology has been selectively applied to microelectronics and a variety of relatively higher priced consumer goods. However, the technology has not been applied in situations where the coating of large quantities of inexpensive objects is required. One such area is the production of coins, coin blanks, discs, medals, tokens, ball bearings, etc. For example, the surface of coins must have an attractive appearance that should be retained for a long time while the coins are in circulation. Thus it is required that the coating exhibit high corrosion and wear resistances.

Recently, there has been a decided push towards the development and usage of gold colored coinage. See, for example, Canadian Patent 1,203,723 and

note the recent introduction of the golden color Canadian dollar coin. The British pound, Australian dollar, French 10 franc and Spanish 100 peseta have also been recently issued in a variety of bronzes.

Experiments dealing with titanium nitride deposition on various coins using a reactive plasma spraying system developed by Multi-Arc Vacuum Systems Inc. of St. Paul, Minnesota have been conducted by applicant. It has been determined that coins of a very attractive golden appearance, which could be retained for at least 20 years in circulation, may be produced by depositing approximately a one micron thick TiN layer on the coins.

Briefly, the PVD system employed for the experiments included a grounded closed chamber (reactor) comprising a pair of negatively charged power supplies (-17.5 volts) communicating with a corresponding pair of metal evaporators (cathodes) disposed within the reactor. When energized, the evaporators (in this case titanium evaporators) emitted a plasma stream of positively charged titanium ions. A fixture table, negatively charged by an external bias supply (-150 to -400 volts) and used for supporting the materials to be coated, was also disposed within the reactor and positioned to be bombarded by the titanium ions. A vacuum pump and means for supplying a reactive gas (such as nitrogen) to the reactor completed the system.

In operation, the titanium ions are attracted to and bond to the table and objects thereon. By introducing the reactive gas into the chamber, the nitrogen and titanium combine on the substrate forming TiN - a hard, corrosion resistant gold colored coating.

However, production problems associated with handling and fixturing the coins were encountered. The slow production rate would be a severe constraint in making the process economically feasible when using the table fixture. The coins to be coated had to be placed on the table in a single layer. During deposition only the upper side of coins (exposed to the Ti cathode) were coated. Therefore following the coating of the exposed coin side, the reactor had to be opened, the coins cleaned and then put on the table with the other side up. The coating process then had to be repeated.

Thus it could be seen that the process was slow, labor intensive and, as a consequence, not economically feasible for use with small objects. The system, as it stood, precluded the economic coating of small parts.

SUMMARY OF THE INVENTION

Accordingly, there is provided an economical technique for coating objects. Storage means, such as a rack adapted to locomote the objects and positioned within a reactor, is disposed between two opposed evaporators.

The rack, capable of holding a large number of

objects, presents a plurality of object sides to the evaporators. By moving the rack (tilting through a predetermined arc in one embodiment), the objects are further rotated to allow full exposure to the plasma streams emanating from the evaporators.

BRIEF DESCRIPTION OF THE DRAWING

Figure 1 is an end schematic view of an embodiment of the invention.

Figure 2 is an elevation of a feature of the invention.

Figure 3 is a cross sectional elevation of an embodiment of the invention.

Figure 4 is a plan view of Figure 3 taken along line 4-4 of Figure 3.

PREFERRED MODE FOR CARRYING OUT THE INVENTION

Referring to Figures 1 and 2 there is shown a coating reactor 10 and an object rack 12 respectively.

The reactor 10 includes a sealable chamber 14. At least two opposed evaporators 16 are disposed toward the interior of the chamber 14 so as to generate charged ionic plasma streams 18 which are accelerated toward the rack 12 (shown in an end view in Figure 1). It is preferred to orient at least two of the evaporators 16 in an opposed parallel fashion on opposite sides of the chamber 14 so as to simultaneously and fully bathe both sides of the objects stored on the rack 12 completely and evenly in the plasma streams 18. Additional evaporators 16 (not shown) may be positioned as necessary.

The evaporators 16 are electrically connected to conventional power supplies 20 and their attendant controls. The rack 12 is electrically connected to a conventional power supply and control 22.

Vacuum pump 24 draws a vacuum in the chamber 14. Reactive gas source 26 provides the appropriate gas such as nitrogen, carbon, oxygen, etc. into the chamber 14.

Figure 2 depicts the object rack 12. In the embodiment shown, the electrically conductive rack 12 consists of an open frame structure 28 having a plurality of parallel spaced races 30 and supporting sides 32. One side 32A of the frame 28 opens to permit the introduction and removal of objects 34 which, in this instance, are coins. A lockable removable slide, hinged member, or similar construction constituting the side 32A, permits entrance and egress from the races 30. The expression "object" shall be construed to include coins, coin blanks, discs, tokens, medals, keys, ball bearings and other similarly dimensioned mass produced products.

The frame 28 is pivotally mounted, via pin 36, on support structure 42. Stops 38 act as limits as the frame 28 is pivoted through arc 40. The support structure 42 electrically communicates with the power supply and control 22.

It was realized that in order to make coating of the

coins 34 economically feasible, both coin sides had to be coated simultaneously. Consequently the rack 12 shown in Figure 2 was developed. The rack 12 loaded, for example, with the coins 34 is located between the evaporators 16 as shown in Figure 1. The spacing of the races 30 is such that the coins 34 can be moved freely while preventing their release from the frame 28. During coating, the rack 12 is oscillated through the arc 40 of about 5 to 10 degrees sideways causing the coins 34 to roll from side to side. The length of the races 30 are longer than the total length of coins 34 in the races 30 so that the space marked "A" in Figure 2 is left between the coins 34 and the side 32 (or 32A). The extent of dimension A is such that as the rack 12 is rotated from side to side the coins 34 are rotated in multiples of quarter turns, i.e., approximately 1/4 or 3/4 or 1-1/4 revolutions. This facilitates coating the entire coin 34 surface. It should be noted that if the coins 34 were not oscillating in the races 30, the coin 34 portions shaded by the races 30 would not be coated. Oscillation of the frame 28 may be caused by any suitable driving mechanism, such as eccentric cams contacting the frame 28, alternating magnetic contacts, reciprocating plungers, etc.

The invention and manner of applying it may be better understood by a brief discussion of the principles underlying the invention.

A number of experiments were conducted to determine the efficacy of the instant technique using the equipment depicted in Figures 1 and 2. For larger scale operations the reactor system 44 shown in Figures 3 and 4 may be employed.

Referring to Figures 3 and 4, the reactor system 44 comprises two connected vessels 46 and 48 divided by baffles 50.

The first vessel 46 is used for storage of the racks 12 and the second vessel 48 is used for coating. As previously discussed, a single rack 12 is coated simultaneously from at least both sides. After the coating process is completed the rack 12 is moved from the coating reactor 48 to the storage vessel 46 and another rack 12 is brought in from the storage vessel 46 to the coating reactor 48. The process is repeated until the desired number of racks 12 are coated. The reactor system 44 is sealed and under a high vacuum during the entire process. The reactor system 44 may accommodate up to thirty or more racks 12. The rack 12 size depends on the size of the reactor employed and the objects to be coated. It is expected that a rack 12 capacity of about 1000 coins is manageable. Thus assuming thirty racks 12 having 1000 coins each, 30,000 coins can be charged into reactor system 44. This improves the productivity of coating to such a degree that the lowered coating cost per coin becomes acceptable.

The manipulation of the racks 12 within the reactor system 44 can be performed automatically on a time preset basis using available driving mechanisms and programmable controllers. The driving mechanisms will index and shuttle the racks 12 within both vessels 46 and 48. Upon introduction into the reactor vessel 48, the rack 12 is oscillated through the arc 40 to ensure complete coating coverage by the plasma streams 18 emanating from the opposed evapora-

tors 16.

The racks 12 are loaded with coins outside the reactor system 44. The loaded racks 12 pass through a cleaning line (not shown) where the coins are cleaned and dried. A plurality of racks 12 are loaded into cassette 58 and are charged into the storage vessel 46 via door 52. Each cassette 58 includes indexing rack 60. The indexing rack 60 is registered against corresponding first pinion 62. The rack/pinion combination 60 and 62 propels the cassette 58 into and out of the storage vessel 46 on support guides 61 and, in addition, by selectively positioning each rack 12 in the appropriate position within the storage vessel 46, ensures that each rack 12 is introduced into the reactor vessel 48.

Each rack 12 includes a lower toothed extension 66 which is sized to contact second pinion 68. After the cassette 58 is indexed to bring a rack 12 coincident with the axis of symmetry 64, the second pinion 68 rotates to draw the rack 12 out of the cassette 58 and pass it over to third pinion 70. Guides 72 and 74 prevent the rack 12 from falling over.

Rotating flipper 76 engages the extension 66 to translate the rack 12 into holding member 86. The member 86 is adapted to accommodate the rack 12. A projection 78 extending from the lower arm of the member 86 is pivotally mounted within support 42A to permit limited oscillatory movement of the member 86 and the rack 12 through the arc 40. Eccentric cam 80 provides the impetus to the member 86.

Upon completion of the process, the indexing technique is reversed so that the rack 12 is reintroduced into the cassette 58. After the cam 80 ceases revolving, the flipper 76 rotates in the opposite direction (counter-clockwise in Figure 3) to hand off the rack 12 back to the third pinion 70 and then ultimately back to the second pinion 68 and home in the cassette 58.

After the rack 12 is safely positioned back within the cassette 58, the first pinion 62 rotates a predetermined distance so as to simultaneously push the cassette 58 and the just treated frame 12 forwardly and place a new rack 12 in position. This indexing, shuttling operation and return cycle is repeated until all of the racks 12 in the cassette 58 have been treated.

Initially, after the cassette 58 is positioned in the storage vessel 46, the reactor system 44 is then sealed and evacuated to the desired pressure (or vacuum). The indexing/shuttling mechanism moves the racks 12 to the center of the storage vessel 46 and then into the coating reactor 48 as discussed above. Micro processors and sensing devices may be utilized to oversee and operate the apparatus and method.

Rotatable water cooled baffles 50, located midway the storage vessel 46 and the coating reactor 48 close. The purpose of these baffles 50 is to prevent the ions from entering the storage vessel 46 during the reacting process which is maintained at a relatively cool temperature by cooling coils 54. It is not desirable to allow stray plasma to contact the components stored in the storage vessel 46.

After proper rack 12 orientation, the oscillating mechanism 80 is energized and a suitably high negative potential is applied to the rack 12. A high current (30-150 amperes) is applied to the evaporators 16. The plasma 18 is initiated by established procedures. As the negative potential is applied to the rack 12 and in the absence of a reacting gas, the coins are sputtered (bombarded) by the titanium or other metal ions.

After the desired sputtering period, which can be about one to five minutes, the rack 12 potential is reduced and the reacting gas (nitrogen in the case of TiN coating) may be introduced into the reactor 48. This initiates the TiN reaction on the coins which may be conducted for about five to sixty minutes. This reactive time depends upon: the desired film thickness to be deposited, cathode or evaporator current, rack (substrate) potential, nitrogen partial pressure, and cathode-substrate distance. During the sputtering and reacting periods the objects 34 are heated during their bombardment by the ions and reacting gas molecules. It is important to select the coating variables within such limits so that the temperature of the objects does not approach their softening point. Otherwise the wear resistance of the coated objects 34 would be reduced.

The coating reactor 48 has at least a pair of opposed parallel evaporators 16 on both sides of the frame 12. The spacing of these evaporators with respect to each other is very important and should be such that it gives a fairly uniform coat of thickness.

For a 1 micron thick TiN deposit, which was found to be sufficient for nickel coinage, the preferred coating conditions are as follows:

Evaporator Current : 30-150 amperes

Substrate (Rack) Potential : 100-400 volts (negative)

Cathode - Substrate Distance : 0.15-0.3 meters

Cathode - Cathode Distance : 0.3-0.6 meters

In order to increase the production rate, it is necessary to minimize the coating time. It has been calculated that the optimal coating time for coinage is about ten minutes.

After the predetermined coating period, the reactive gas, the evaporator current, the rack potential, and the oscillating mechanism 80 are shut off. The rack 12 is removed from the coating reactor 48 and reintroduced into the storage vessel 46 after opening the baffles 50 as discussed above.

Then a second rack 12 is brought from the storage vessel 46, placed into the coating reactor 48 and the cycle is repeated.

When all of the racks 12 have been coated, the reactor system 44 is vented and opened. The cassette 58 is unloaded via door 56 and the system is cleaned of Ti and TiN dust. Then a new set of object loaded racks 12 is charged into the storage vessel 46 and the process begins anew.

A number of experiments utilizing the apparatus depicted in Figures 1 and 2 confirmed the efficacy of the instant technique. The rack 12 was oscillated manually.

EXAMPLE 1

A rack 12 loaded with Canadian \$1 blanks (made of nickel) was coated under the following conditions:

Evaporator Current : 90 amperes

Evaporator - Substrate (Coin) Distance : 0.305 meters

Substrate Potential : -100 volts

Coating Time : 30 minutes

N₂ Pressure : 1.74 newtons/meter²

No. of Evaporators/ft² (0.1m²) of Substrate area : 1 per each side

Maximum Coating Temperature : 800°F (427°C)

Approximately a one micron thick layer of TiN was deposited which had a very attractive golden appearance.

The produced coins were tested for wear using a tumbling product tester. After fourteen days of continuous testing, which is equivalent to about eighteen years of a normal circulation wear, the coins retained an attractive golden appearance.

EXAMPLE 2

Various other coins were coated using the rack 12 at variable conditions:

Evaporator Current : 20-150 amperes

Evaporator Substrate Distance : 0.15-0.395 meters

Substrate Potential : -100 to -400 volts

Coating Time : 10-120 minutes

N₂ Pressure : 1-10 newtons/meter²

In summary, all coins or blanks of nickel origin showed very attractive golden appearance after TiN coating and exhibited a superior wear resistance to non-coated pieces.

It should be noted that although the examples and the drawings relate to nickel coins, the invention is not restricted to any particular object or material. Many different mass produced objects may be coated by this invention, such as ball bearings, keys and other small parts. The rack should understandably be altered to suit the particular object being coated. For example, the racks may be of different shape and spiralled for coating ball bearings. This would allow the ball bearings to be fully rotated. For coating keys the racks could have hanging pins. Another alternative would have the objects disposed along a high receptacle and caused to travel downwardly through a vertically oriented twisted and/or serpentine race into a lower receptacle. This scheme, utilizing gravity, would cause the objects to be evenly exposed to the plasma stream 18.

Additionally the invention is not restricted to TiN deposition since it is applicable to other coating materials. For example, other metallic coatings which are amenable to reactive plasma coating, such as TiC, ZrN, HfN, TaN, TiAlN, etc. may be employed.

In addition, the instant invention may be used for applying elemental coatings onto the objects, without the use of a reactive gas. For example, coatings of Ti, Zr, Ta, Al, Cr, etc. may be applied by

evaporating them onto the objects disposed on the racks.

It should also be appreciated that other means can be provided to shuttle and index the racks into and out of the reactor vessel. For instance, a two-chamber device with a valve disposed therebetween can be used. In this arrangement the first chamber acts as a vacuum lock and the second chamber acts as the reactor and only two racks are present in the apparatus at any one time. Moreover, overhead travelling hooks, piston actuated grabbing arms, screw drive draws, etc. may be utilized to position and index the frames 12 within the vessels. Applicant does not wish to be limited to the specific positioning, indexing, and oscillatory embodiments depicted herein.

In the method of the present invention: (i) it is preferred that the objects are subjected to ion plasma fluxes emanating from at least two opposed ion plasma evaporators and preferably the surface of each object is simultaneously bombarded by the plasma stream from at least two opposite directions; (ii) the storage means may electrically communicate with a power supply; (iii) the storage means may permit the objects to rotate in order to expose their surface area to the plasma flux and preferably the objects are rolled in multiples of a quarter turn; (iv) the storage means can include a frame, at least one race (but preferably a plurality of races) adapted to allow movement of the objects disposed therein, and means for gaining access to the race(s); (v) the method may include steps wherein the objects are (a) loaded into the storage means and prepared for coating in at least one location, (b) transported to the reacting area, (c) simultaneously subjected to the ion flux and rotationally locomoted within the reacting area, and (d) removed from the reacting area and the storage means and during these steps, the objects may be subjected to a reacting gas, e.g. nitrogen, carbon or oxygen; (vi) the objects may be metallic objects, e.g. coins, blanks, tokens, discs, medals and ball bearings; (vii) the plasma flux may include titanium, zirconium, tantalum, aluminium or chromium; (viii) the objects coated by the method preferably have a golden appearance.

In the system of the present invention: (i) the storage means may be disposed in the chamber so as to expose the objects to two opposed ionic plasma streams, (ii) separating means may be provided, e.g. temperature regulated baffles, between the storage means and the reactor chamber, (iii) means may be provided for moving and positioning the storage means within the storage vessel and/or for moving and positioning the storage means within the reactor chamber; (iv) the system may include means for transporting and positioning the storage means between and within the storage vessel and the reactor chamber; (v) the system may be used to coat small mass-produced products, e.g. coins, blanks, tokens, discs, medals and ball bearings.

The present invention also provides an electrically conductive rack for coating objects disposed therein by vapor deposition techniques, the rack comprising a frame, at least one object race within

the frame for allowing rotational movement of the objects, means for permitting the introduction and removal of the objects into the race, and the rack adapted to be situated within at least one ionic plasma stream; the rack may also include means for causing rotational movements of the objects therein.

5

means.

10. The system according to claim 9 include a cassette and wherein the storage means is disposed within the cassette and the system includes means for selectively engaging and moving a storage means into and out of the cassette.

Claims

10

1. A method for coating objects, the method comprising:

a) introducing the objects into a storage means;

15

b) situating the storage means in a reacting area before at least a plurality of ion plasma evaporators;

c) rotationally locomoting the objects within the storage means;

20

d) subjecting the locomoting objects to an ion plasma flux generated by the ion plasma evaporators, causing the ions to bond to the objects; and

25

e) removing the objects from the storage means.

2. The method according to claim 1 further comprising causing a gas to react with the ions disposed on the surface of the objects generating a coating thereon.

30

3. The method according to claim 1 wherein the storage means is oscillated through an arc to cause the locomotion of the objects.

4. The method according to claim 2 when the resultant coating is selected from the group consisting of TiN, TiC, ZrN, HfN, TaN, TiAlN, TiO₂, ZrO₂, HfO₂ and Ta₂O₅.

35

5. A system for plasma coating objects, the system comprising a sealable reactor chamber, means for introducing at least one ionic plasma stream into the reactor chamber, an object storage means disposed within the reactor chamber and adapted for rotationally locomoting the objects within the ionic plasma stream, and means for controlling the plasma stream.

40

45

6. The system according to claim 5 including means for introducing a reactive gas into the chamber and/or means for oscillating the object storage means through a predetermined arc in the reactor chamber.

50

7. The system according to claim 5 including means for supplying at least two opposed ionic plasma streams into the chamber.

8. The system according to claim 5 wherein the storage means includes a frame, the frame, having at least one race, the frame adapted to allow movement of the objects within the race, and means for gaining access to the race.

55

9. The system according to claim 5 including a storage vessel communicating with the reactor chamber, means for transporting the storage means from the storage vessel to the reactor chamber and back again, and means for locomoting the objects within the storage

60

65

FIG. 1

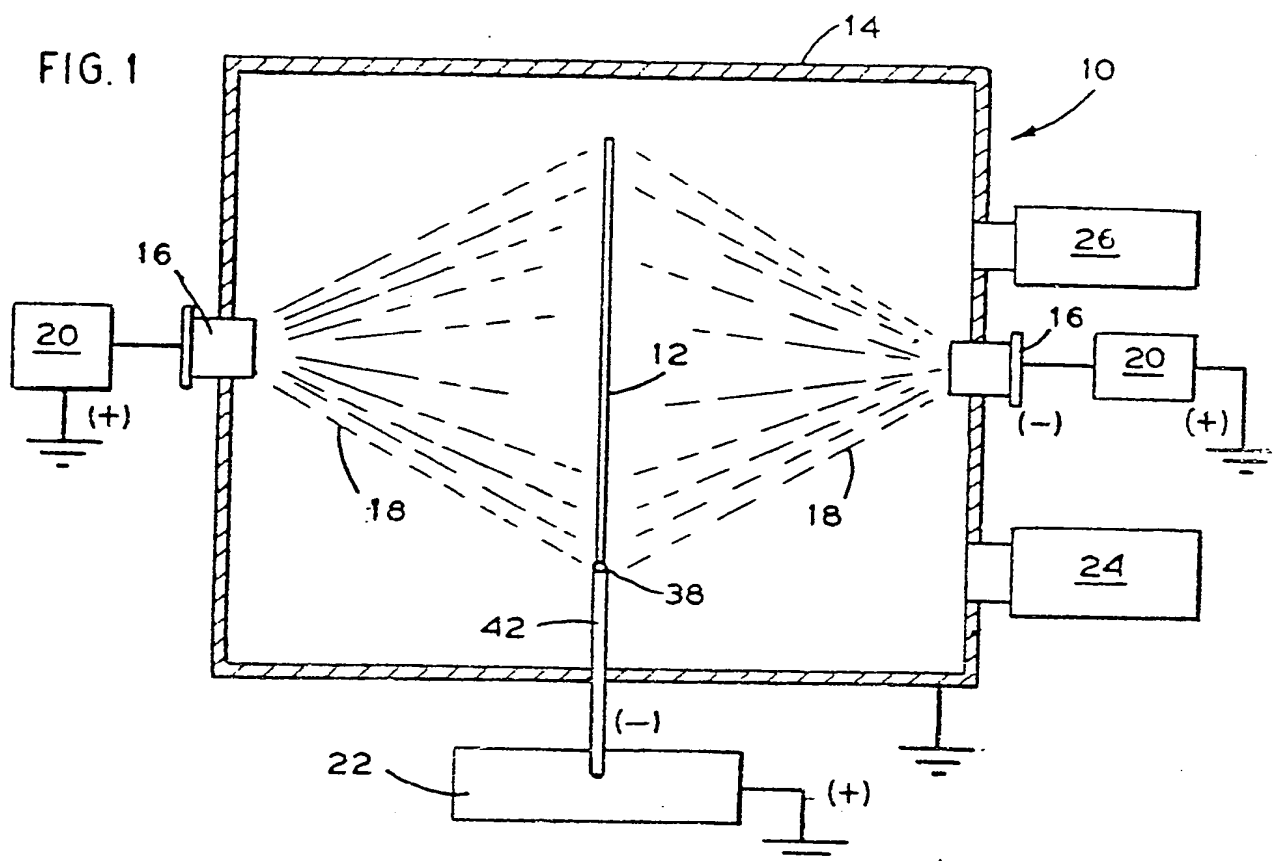
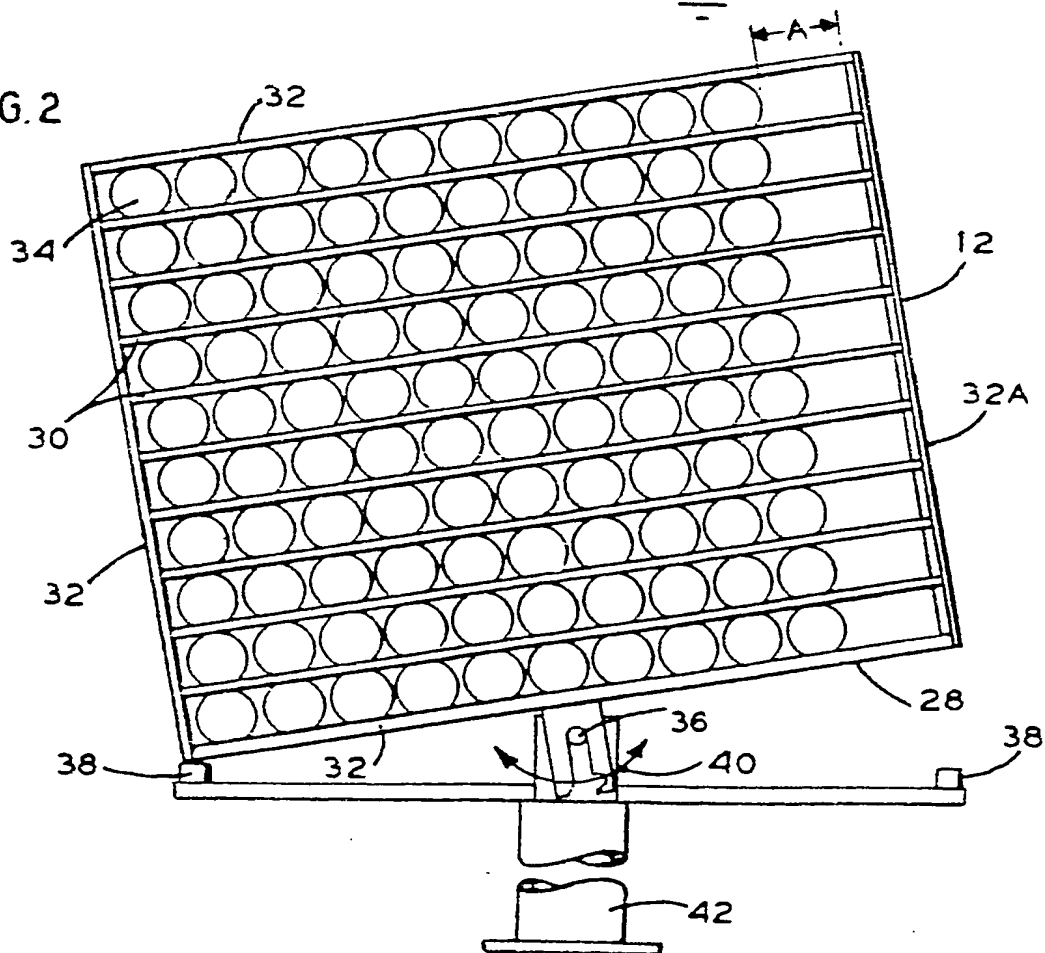
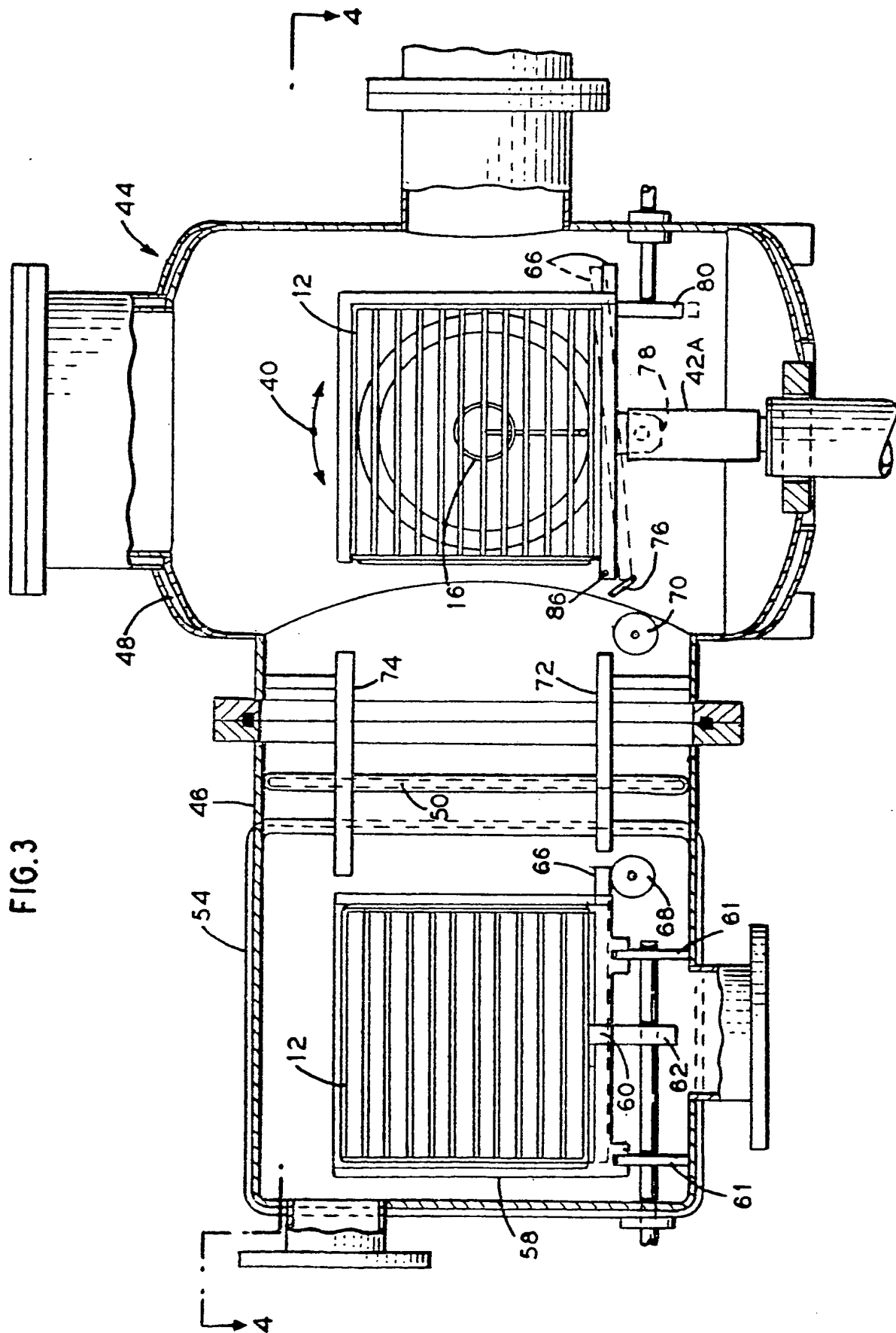
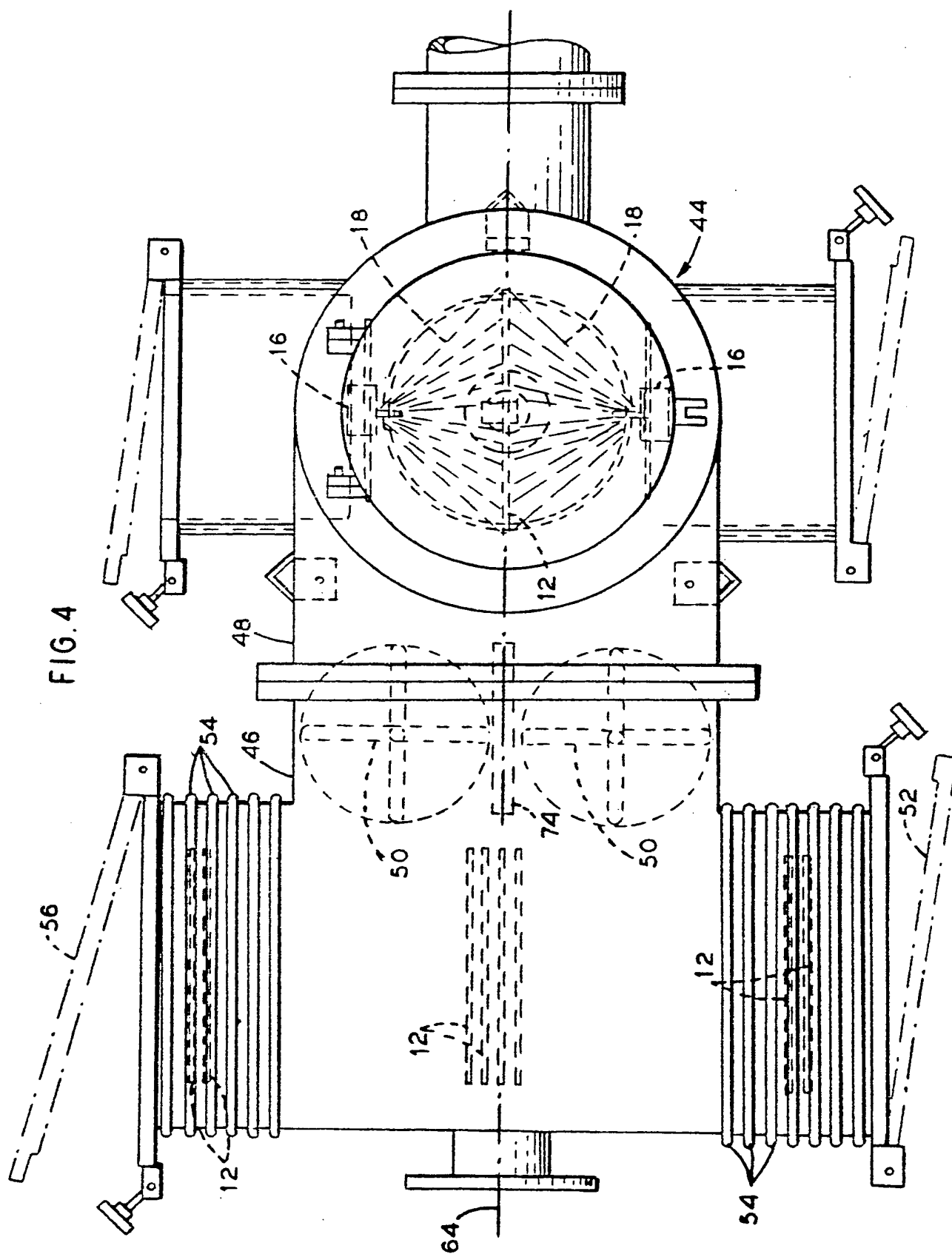


FIG. 2









⑫

EUROPEAN PATENT APPLICATION

⑳ Application number: **88304837.3**

⑤① Int. Cl.⁴: **C 23 C 14/32**
C 23 C 14/56
// A44C21/00

㉔ Date of filing: **27.05.88**

③① Priority: **29.05.87 CA 538430**

④③ Date of publication of application:
30.11.88 Bulletin 88/48

⑥④ Designated Contracting States:
AT BE CH DE ES FR GB GR IT LI LU NL SE

⑥⑧ Date of deferred publication of search report:
30.08.89 Bulletin 89/35

⑦① Applicant: **INCO LIMITED**
Royal Trust Tower Toronto-Dominion Centre
Toronto Ontario, M5K 1N4 (CA)

⑦② Inventor: **Bell, James Alexander Evert**
3217 Shoreline Drive
Oakville Ontario, L6L 5Y9 (CA)

Conard, Bruce Randolph
153 Balsam Drive
Oakville Ontario, L6J 3X4 (CA)

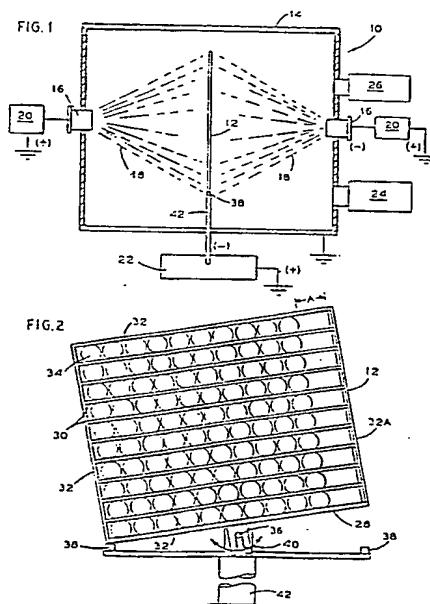
Babjak, Juraj
671 Louis Drive
Mississauga Ontario, L5B 2V4 (CA)

Bradford, Raymond Augustus
216 Andrew Park
Woodbridge Ontario, L4L 1G5 (CA)

⑦④ Representative: **Hedley, Nicholas James Matthew et al**
TZ Gold & Company 9 Staple Inn
London WC1V 7QH (GB)

⑤④ **Apparatus and process for coloring objects by plasma coating.**

⑤⑦ A technique is provided for presenting and fixturing small items that are coated by vapor deposition techniques. The objects (34) are held in a rack (12) that is held in a plasma stream (18). The objects are caused to be moved within the rack (12) to effect full coverage by the plasma stream. The coating, if titanium nitride, is gold colored and is, for example, useful for coinage applications.





EP 88 30 4837

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
X	US-A-3 926 147 (K.E. STEUBE) * Claims 1-8; figures 5,6; page 7, lines 33-68; page 8; page 9, lines 1-52 * ---	1-3,5,6	C 23 C 14/32 C 23 C 14/56 // A 44 C 21/00
X	FR-A-2 423 551 (NIHON SHINKU GIJUTSU) * Claim 1; figures 1,2; page 2, lines 34-38; page 3, lines 1-20 * ---	1,5	
A	PATENT ABSTRACTS OF JAPAN, vol. 8, no. 67 (C-216)[1504], 29th March 1984; & JP-A-58 217 674 (CITIZEN TOKEI K.K.) 17-12-1983 * Abstract * ---	1,5	
A	XEROX DISCLOSURE JOURNAL, vol. 9, no. 3, May/June 1984, pages 173-175, Xerox Corp., Stamford, Connecticut, US; G.P. CEASAR et al.: "Multiple drum fabrication for ion beam deposited a-Si:H photoreceptors" * Whole document * ---	1,5	
A	FR-A-2 412 620 (NIHON SHINKU GIJUTSU) * Figure 1; page 4 * ---	4	
A	PATENT ABSTRACTS OF JAPAN, vol. 5, no. 98 (C-60)[770], 25th June 1981; & JP-A-56 41 375 (MATSUSHITA DENKI SANGYO K.K.) 18-04-1981 * Abstract * ---	2,6	
A	FR-A- 979 772 (A. HUWYLER) * Claims; figure 1 * ---	7	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 07-06-1989	Examiner ELSEN D.B.A.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document			

EPO FORM 1503 03.82 (7/0401)



European Patent
Office

EUROPEAN SEARCH REPORT

Page 2

Application Number

EP 88 30 4837

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	US-A-2 746 420 (K.H. STEIGERWALD) * Figures 1,2; claims 1,22,29,30; page 6, lines 9-11; page 7, lines 19-26; page 8, lines 31-36 *	9	
X,P	DE-U-8 711 193 (INTERATOM) * Abstract; figure 1 *	1,5,7	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 07-06-1989	Examiner ELSEN D.B.A.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1503 03.82 (P0401)

